

On the Problem of the Nature of the Effect of Complex
Catalysts of the Reaction of Polymerization of Vinyl Compounds.

20-4-25/52

black residue. The ampules were put into a thermostat and the separating wall was broken after equalization of temperature. The most important conditions and results of the tests are compiled in two tables. The pure monomers are polymerized by three of the catalysts specified here, but not by triethyl-aluminium. The polymerization of α -methylstyrol by ethyl-lithium takes place only slowly. With the copolymerization of an equimolecular mixture of polymers the copolymer (sopolimer) which is in the initial stage must contain 60% styrene-members and 40% α -methyl-stirol-members. Based upon the composition of the developping copolymers, the complex catalysts must be computed to the type of acid-catalysts. This is also indicated by the fact that with the presence of complex catalysts no polymerization of methylmethacrylate and acrylonitrile takes place. The difference between the complex and acid catalysts is supposed to consists in the structural peculiarities of the heterogeneous catalyst. With the complex catalysts it is very likely - on account of their crystalline structure - that the adsorbed molecules of the monomer react with the active center on the surface of the catalyst. Such a hypothesis explains the rules governing polymerization by

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Catalysts of the Reaction of Polymerization of Vinyl Compounds.

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complex catalysts, as observed by various authors.
There are 2 tables and 12 references, 2 of which are Slavic.

ASSOCIATION: Institute of High-Molecular Compounds AN USSR (Institut
vysokomolekulyarnykh soyedineniy Akademii nauk SSSR).

PRESENTED: May 23, 1957, by V. A. Kargin, Academician.

SUBMITTED: May 15, 1957

AVAILABLE: Library of Congress

Card 3/3

AUTHORS: Rakova, G. V., Korotkov, A. A. 20-119-5-39/59

TITLE: Investigation of the Copolymerization of Isoprene and Divinyl
by Butyl Lithium (Issledovaniye sopolimerizatsii izoprena i
divinila butillitiyem)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 119, Nr 5,
pp. 982 - 985 (USSR)

ABSTRACT: The determination of the relative reactivity of the diethylene-
-hydrocarbons isoprene and divinyl (which are distinguished only
by the existence of a methyl group) in the case of catalytic
basic copolymerization. The composition of the copolymers was
determined by means of the method of marked atoms. For this pur-
pose isoprene was synthesized with C¹⁴ according to a somehow
modified method by A. Ye. Farovskiy (Reference 7). All opera-
tions were carried out in a current of dry nitrogen or in
vacuum. The polymerization reaction was interrupted at differ-
ently progressed stages of the transformation by quick cooling
of the reaction ampoule. Then the ampoules were opened and a
little (2 ml) ethylalcohol was added to decompose the catalyst.
The compositions of the copolymers were determined by the radio-
activity of the samples. The results of the experiments were

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Investigation of the Copolymerization of Isoprene and
Divinyl by Butyl Lithium

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compiled in a table. The obtained data make possible the computation of the copolymerization from the exact integral equation by F. R. Mayo and F. M. Lewis (L'yuis) (Reference 9). For isoprene $\alpha = 0,47 \pm 0,03$ and for divinyl $\beta = 3,38 \pm 0,14$ are found. Two diagrams show the computed curves for the copolymers which also contain the experimental points. The compositions of the copolymers with given initial conditions of the monomers were computed graphically according to a method mentioned. The experimental points satisfyingly fit on the computed curves. From the experimental data mentioned the following can be concluded: 1) In common copolymerization divinyl is the more active polymer. 2) In separate polymerization isoprene is more active. 3) In common polymerization the reaction velocity in the initial stage corresponds to the velocity of the separate polymerization of divinyl. There are 3 figures, 1 table and 10 references, 4 of which are Soviet.

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Investigation of the Copolymerization of Isoprene and Divinyl by Butyl Lithium 20-119-5-39/59

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR
(Institute for High Molecular Compounds AS USSR)

PRESENTED: December 16, 1957, by A. V. Topchiyev, Member, Academy of Sciences, USSR

SUBMITTED: December 16, 1957

Card 3/3

KROTKOV, A. A.

(Hd., Inst. Macromolecular Compounds, Acad. Sci. USSR)

"Kinetics and Mechanism of Polymerization of Vinyl Monomers by Metallo-organic Compounds,"

paper presented (by Prof. S. E. Bresler) at the Gordon Conference on Polymer Research
New London, New Hampshire, 30 June - 4 July 1958.

Discussion - B,3,113,847.

AUTHOR: Korotkov, A., Deputy-Director

4-58-5-20/41

TITLE: Difficult Research (Trudnyy poisk)

PERIODICAL: Znaniye - sila, 1958, Nr 5, p 25 (USSR)

ABSTRACT: The author tells of the difficulties experienced in obtaining synthetic caoutchouc for general use and of the Soviet researches that have led to obtaining a polymer from the molecules of izoprene, which by its composition is identical and by its microstructure comes very near to natural caoutchouc. In the synthesis of polymers of the given microstructure, science has developed to such an extent where the production of synthetic caoutchouc, which will be superior to natural caoutchouc in every respect, will soon to be realized. The author mentions the name of Academician S.V. Lebedev, according to whose method hundreds of thousands of tons of synthetic caoutchouc have been manufactured since 1932.

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Difficult Research

4-58-5-20/41

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR
(Institute of High-Molecular Compounds, USSR Academy of
Sciences)

Card 2/2 1. Synthetic rubber--Sources 2. Polymers--Applications 3. Polymers
 --Synthesis

KOROTKOV, A. A.

AUTHOR: Bresler, S. Ye., Korotkov, A. A., Mosevitskiy, 57-1-16/30
M. I., Poddubnyy, I. Ya.

TITLE: Investigation of Catalytic Polymerization of Diene
Hydrocarbons by Means of Molecular-Weight Distribution
of Polymers (Issledovaniye kataliticheskoy polimerizatsii
diyenovykh uglevodorodov s pomoshch'yu molekulyarno-vesovykh
raspredeleniy polimerov)

PERIODICAL: Zhurnal Tekhnicheskoy Fiziki, 1958, Vol. 28, Nr 1,
pp. 114-131 (USSR)

ABSTRACT: The problems in connection with the computation and the
analysis of the theoretical molecular-weight distribution
are investigated. On the basis of the analysis the ex-
perimental data are discussed which are obtained on the
occasion of the production of polyvinyl and polyisoprene
samples by means of polymerization in a solution under the
action of lithium-butyl. Lithium-buthyl had been chosen as
catalizer because it is soluble in saturated hydrocarbons
due to which fact polymerization is homogeneous and the
analysis of the results is considerably easier. The
theoretical computation and the analysis of the molecular

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of Polymers

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weight distribution can be carried out according to 2 methods. Considering the discrete polymerization process i.e. the connection of a sequence of monomer units with the growing chain, a system of differential equations can be set up. The problem can be solved by means of this system. However, this solution expressed in sums is somewhat complicated. If, however, from the beginning polymerization is approximated by the assumption of a continuous increase of the chain, a much simpler problem with a very convenient solution is obtained. However, in this case some details get lost. Both methods of computation are given. Divinyl and isoprene are used as monomers and on the occasion of the polymerization hexane and diethyl-ester are used as solvents. The measuring of the polymerization kinetics was carried out according to the dilatometric method. The sedimentation experiments were carried out in the ultra centrifuge of Svedberg (ref. 14) with scale optics at 60000 - 65000 rev./min. The diffusion tests were carried out in the Lamm apparatus with scale optics (ref. 14) at $(20 \pm 0,003)^{\circ}\text{C}$. It is demonstrated

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carbons by means of Molecular-Weight Distribution of Polymers

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that on the occasion of polymerization of divinyl or isopren with lithium butyl in hexane at 30 - 70°C the role of the secondary reactions which lead to the limitation of the growing of the chain is only unimportant and that it can be neglected. I.e. nearly all active chains grow until the complete utilization of the monomer. On the occasion of the polymerization the author observed a similar occurrence to that described in reference 20 and 21 by one of the authors. It is demonstrated that a delay in the growing of the polymer molecules due to interaction of the polar active centres counteracts simultaneously to the increase of the general polymerization-velocity with increase of the concentration of the active centres. With the increase of the polymerization-temperature the role of the heat movement becomes more important. The shape of the curves of the molecular-weight-distribution shows that on the one hand the formation of a complex with ester activates the binding to which the monomer units are connected with the active complex from the catalytical point of view, on the other hand, however, that it weakens them. For this reason a break in this connection is

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possible and it is accompanied by the separation of a complex from the polymer chain. Furthermore, it is demonstrated that the hydrodynamic properties of the macromolecules depend only little on the micro structure of the molecular chains. It seems to be due to the following reason: the increase from one member to two members with simultaneous shortening of the chain causes a decrease of the mobility of the individual members due to which fact the measurements of the molecular ball in the solution remain practically unchanged. The second very important conclusion is that the rise of the polymerization temperature to 70°C, as well as the use of ester as solvent lead to no important increase in the branching of the molecular chain since the presence of a uniform dependence $S=d(M)$ for the polymer type concerned is very unlikely. Analytic dependence of S and M in the molecular weight interval (S in Svedberg): for polydivinyl in octan at 20°C... $S = 0,0389 \cdot M^{0,39}$, for polyisopren in octane at 20°C... $S = 0,0155 \cdot M^{0,49}$. M. N. Barsukova assisted at this work. The work was discussed with S. Ya. Frenkel'. There are 15 figures, 1 table, and 25 references, 6 of which are Slavic.

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Investigation of Catalytic Polymerization of Diene Hydrocarbons by Means of Molecular-Weight Distribution of Polymers

57-1-16/30

ASSOCIATION: Institute for High-Molecular Alloys AN USSR Leningrad
(Institut vysokomolekulyarnykh soyedineniy AN SSSR, Leningrad)

SUBMITTED: July 23, 1957

AVAILABLE: Library of Congress

Card 5/5

~~KORSEK~~ KOROTKOV A.A.

3-9-19/31

AUTHOR: None Given

TITLE: Inter-vuz Scientific Conferences (Mezhvuzovskiy nauchnyye konferentsii)

PERIODICAL: Vestnik Vysshey Shkoly, 1957, # 9, pp 73 - 76 (USSR)

ABSTRACT: In January 1957, the Second All-Union Conference on Photosynthesis took place, organized by the Institute of Plant Physiology of the Academy of Sciences, USSR, and by the Faculty of Soil-Biology of the Moskva University. About 700 representatives of 130 scientific-research institutes, vuzes and ministries were present. The introductory report was made by Academician A.L. Kursanov who described the development of photosynthesis during the last ten years and invited the scientists to concentrate their work on the application of radioactive and stable isotopes. Nearly 100 reports were read: 13 on photochemistry, 9 on the investigation of chloroplast structure, 19 on the investigation of pigments, 9 on the photosynthesis of water plants, bacteria, etc.

Reports on the results reached in the field of photosynthesis were made by: Doctor G. Polster from the German Democratic Republic, Professor N. Seledzhanu from the Rumanian People's Republic, Professor K. Popov from the Bulgarian People's Republic. Finally the Conference stated the great role of Soviet scientists in the development of photosynthesis and gave some defi-

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Inter-vuz Scientific Conferences

ciencies in the research organization, in particular, the insufficient participation of biologists in the solution of the problem in question.

The Ninth Conference on High-molecular Combinations took place from 28 January to 1 February. It was organized by the USSR Academy of Sciences and the MGU and concentrated on general matters of polymeric chemistry and physics. About 1500 scientists were present from 172 organizations and 37 towns of the Soviet Union, the representatives of 42 vuzes and 17 foreign scientists from China, East Germany, Poland, Rumania, Czechoslovakia, Yugoslavia, the German Federal Republic and Israel.

The introductory speech was made by Academician V.A. Kargin, who described the present state of science relating to polymers, and invited the scientists to concentrate their work on new methods of obtaining polymers, and new classes of high-molecular substances. In the section of polymeric synthesis 43 papers were read. The author enumerates the following reports: Academician A.N. Nesmeyanov on the reaction of ethylene polymerization and carbon tetrachloride.

S.S. Medvedev, Member-Correspondent of the USSR Academy of Sciences, on the kinetics of various types of polymerization.

Professor B. A. Dolgoploska (Leningrad) on the initiation of radical polymerization.

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Korotkov, A.A.

Inter-vuz Scientific Conferences

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~~A.A. Korotkov~~ (Leningrad) on catalytic polymerization.
~~V.V. Korshak~~, Member-Correspondent of the USSR Academy of Sciences (Moscow) on syntheses of phosphor containing polymers.
Professor G.Kh. Kamay (Kazan') on syntheses of certain unsaturated ethers of phosphinous acids.
Academician O. Vikhterle and Professor Vesely (Czechoslovakia) on cation polymerization of olefines.
K.A. Andriyanov, Member-Correspondent of the USSR Academy of Sciences (Moscow) on the elaboration of a new class of thermally stable polymers.
Professor Z.A. Rogovin on the qualities of methyl carbonic ether of celluloses.
Professor V.I. Ivanov on cellulose qualities and their application in chromatography.
Professor Van-Yu- Khay (China) on the titration of terminal groups of polycaprolactams.
Academician V.A. Kargin (Moscow) and G.S. Markova on the orientation and crystallization of polymeric chains and their disposition.
Academician P.A. Rebinder (Moscow) and Professor G.V. Vinogradov on methods characterizing the viscous elastic qualities

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of polymeric solutions and the application of new rheological and optical polarization methods.

Professor K. Hess (Gess) from the Federal German Republic, on submicroscopic structures of polymers.

Yu. S. Lazurkina (Moscow) and Ye.V. Kuvshinskiy (Doctors of Physics-Mathematics) on the qualities of polymeric glass and the mechanics of glass formation of high molecular combinations.

Professor Chen-Bao-Kun (China) on viscous plastic qualities of natural rubber.

Professor S. Goreyko (Poland) on polyvinyl chloride qualities.

Professor Z.A. Rogovin on investigations in obtaining fluorine containing synthetic carbon chain fibres.

Professor Kh. Simionesku (Rumania) on fractionation of cellulose.

Professor T. Rabek (Poland) on the qualities of ion-exchange resin.

The second Vuz Conference on Embryology took place from 28th January to 5th February at the Moskva University. About 600 participants were present, and 150 reports were read. Present also were Professor G. Muller (Halle, GDR) and A. Kelyus (Krakow, Poland).

The resolution of the Conference contained recommendations to increase theoretical work on the problems of individual develop-

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Inter-vuz Scientific Conferences

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ment of organisms. The creation of an embryology periodical was suggested.

The Moscow University convened the first Vuz Conference on Biochemical and Physico-chemical Principles of the Biological Action of Radiation in February 1957. About 700 participants were present.

An introductory paper was read by Professor B.N. Tarusov (Moscow) dealing with the biological action of ionizing radiations. Professor A.M. Kuzin made a report on radiotonal biochemical aspects. Other reports were:

Professor M.N. Meysel' (Moscow) on the effect of radiation on various components of the cells of micro-organisms. N.P. Dubinin, Member-Correspondent of the USSR Academy of Sciences (Moscow), on radiation genetics.

The resolution of the conference dealt with the creation of a course in radiation genetics, to be included into the program of genetics and biophysics. The conference decided moreover to invite qualified specialists to investigate the biological action of radiation. It was decided to apply at the Ministry of Higher Education for the organization of courses dealing with working methods of isotopes.

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Inter-vuz Scientific Conferences

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A scientific conference dealing with problems of the structure of organic combinations, took place from 14th to 16th January 1957 at the Kazan' University. More than 200 participants were present and 19 reports were delivered on subjects of theoretical organic chemistry (tautomerism, geometry of organic molecules, etc). The conference stated the successful development of the theory of A.M. Butlerov, and the necessity to resolve problems of modern organic chemistry through physical research methods, such as infrared spectroscopy, spectroscopy of the combined dispersion of light and the methods of magnetic resonance, introduced by Ye.K. Zavoyskiy.

A conference on the Economical Efficiency of New Techniques in Construction was convened in January 1957 by the Moskva Institute of Engineering and Economy, together with the economic departments of Gosstroy SSSR and the Scientific-Technical-Society of the USSR Construction Industry. About 430 participants heard 46 reports. Professor, Doctor of Technical Sciences, L.I. Onishchik (Moscow) spoke on "Problems of Wall Building From the Point of View of Economical Efficiency".

Professor Ye.I. Varenik, Doctor of Technical Sciences (Moscow), spoke on "The Evaluation of the Economical Efficiency of Constructions With Selected Sections".

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S/076/63/037/002/001/018
B101/B186

AUTHORS: Korotkov, A. A., Marandzheva, Ye. N. (Moscow)

TITLE: Thermochemical study of the catalytic polymerization of isoprene. I. Thermal effect of the polymerization reaction of isoprene with butyl lithium

PERIODICAL: Zhurnal fizicheskoy khimii, v. 37, no. 2, 1963, 257-264 ✓

TEXT: To clear up inconsistencies in published data on the thermal effect of isoprene polymerization, this effect was determined directly by calorimetry using an apparatus similar to that of L. Tong, W. Kenyon (J. Amer. Chem. Soc., 67, 1278, 1945; *ibid.*, 69, 1402, 1947). The 50% solution of isoprene in gasoline fraction (b.p. 50-60°C) was polymerized at 35 or 61.3°C with 0.013-0.110 mole/l butyl lithium. In the polymerization at 35°C, ether was used as calorimeter liquid. Results: The thermal effect of the polymerization of isoprene dissolved in gasoline with butyl lithium is 15.7 ± 0.4 kcal/mole. In two tests the molecular weights of the polymer were 31,500 and 39,300 and the yields 53 and 63%. The degree of unsaturation was 102%, the content of 1,2 and 3,4 links was 7%. The incomplete polymerization is explained by termination caused by impurities
Card 1/2

POZAMANTIR, A.G.; KOROTKOV, A.A.; LISHANSKIY, I.S.

Catalytic polymerization of olefins. Part 3: Effect of the Ziegler catalyst composition on the molecular weight of polyethylene.

Vysokom.soed. 3 no.12:1769-1773 D '61. (MIRA 15:3)

1. Okhtinskiy khimicheskiy kombinat i Institut vysokomolekulyarnykh soyedineniy AN SSSR.

(Polyethylene) (Catalysts)

FOROTKOV, A.A.; NEPYSHNEVSKIY, V.M.

Synthesis of trialkylaluminum from aluminum halides and lithium
organic compounds. Plast.massy no.6:46-48 '64.

(MIRA 18:4)

KOROTKOV, A.A.; CHESNOKOVA, N.N.; TRUKHMANOVA, L.B.

Catalytic polymerisation of isoprene with butyllithium. *Vysokom.*
soed. 1 no.1:46-57 Ja '59. (MIRA 12:9)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo
kauchuka i Institut vysokomolekulyarnykh soedineniy AN SSSR.
(Isoprene) (Lithium)

KOROTKOV, A.A.; SHIBAYEV, L.A.; PYRKOV, L.M.; ALDOSHIN, V.G.; FRENKEL',
S.I.

Synthesis and study of hybrid polymers. Styrene and isoprene
block-polymers obtained by catalytic polymerization in a solution
under the action of butyllithium. Vysokom. soed. 1 no.3:443-454
Mr '59. (MIRA 12:10)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR.
(Styrene) (Isoprene)

POZAMANTIR, A.G.; KOROTKOV, A.A.; LISHANSKIY, I.S.

Polymerisation of olefins by catalyst complexes. Part 1: Interaction of alkylaluminum chlorides and triethylaluminum with titanium tetrachloride. Vysokom.sped. 1 no.8:1207-1213 Ag '59. (MIRA-13:2)

1. Okhtinskiy khimicheskiy kombinat i Institut vysokomolekul-yarnykh soedineniy AN SSSR.
(Olefins) (Aluminum organic compounds)
(Titanium chloride)

KOROTKOV, A.A.; MITSINGENDLER, S.P.; KRASULINA, V.N.; VOLKOVA, L.A.

Synthesis of polymethyl methacrylate of regular structure. Vysokom.
soed. 1 no.9:1319-1326 S '59. (MIRA 13:3)

1. Institut vysokomolekulyarnykh soedineniy AN SSSR.
(Methacrylic acid)

5.3300

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SOV/80-32-10-40/51

AUTHORS: Lishanskiy, I. S., ~~Korotkov, A. A.~~, Andreyeva, G. A.,
Zak, A. G.

TITLE: Brief Communications. Concerning the Dehydration of
n-Pentanol Over Aluminum Oxide

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Vol 32, Nr 10,
pp 2344-2346 (USSR)

ABSTRACT: Dehydration of aliphatic alcohols over Al_2O_3 leads to
the formation of isomeric olefins. Dehydration of n-pen-
tanol can give 5 possible isomeric pentenes with a boil-
ing range between 20 and 38°. Isolation of pentene-1
is very difficult. Attempts were made to prepare pentene-1
by dehydration of n-pentanol accompanied by the least iso-
merization. Two catalysts were used: a catalyst which
was used for the dehydration of isopropyl alcohol at
360° and afterwards regenerated with air at 450° for
2 hr, and a freshly prepared catalyst. The activity of
both catalysts was the same with respect to the total
hydrocarbon yield. Pentene-1 content in the mixture

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SOV/20-126-3-34/69

AUTHORS: Rakova, G. V., Korotkov, A. A., Corresponding Member AS USSR,
Li Tsung-Ch'ang

TITLE: A Study of the Copolymerization of Isoprene With Piperylene
and Diisopropenyl (Issledovaniye sopolimerizatsii izoprena
s piperilenom i diizopropenilom)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 3,
pp 582 - 585 (USSR)

ABSTRACT: The authors continue here their work (Refs 1,2) on the co-
polymerization of divinyl and isoprene. Isoprene marked with C¹⁴
was also used here. The method is described (Refs 1,2). Figure
1 shows the kinetic polymerization curves of piperylene and di-
isopropenyl. Figure 2 presents these curves for separate and
common polymerization at 50°. Figure 3 shows computed composi-
tion integral curves of the copolymers of the two systems
mentioned in the title. Table 1 shows the test results of co-
polymerization of isoprene and piperylene in hexane at different
temperatures and with a diethyl-ether admixture at 60°. The
authors conclude from the results: if in the copolymerization
of isoprene with divinyl an activity "reversal" takes place,
and if on account of the data on separate polymerization the
composition of the occurring copolymer cannot be predicted, the

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A Study of the Copolymerization of Isoprene With
Piperylene and Diisopropenyl

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relative activity of the monomers is maintained in the cases discussed here both in separate and common polymerization. It can be expressed by the series: isoprene \gg piperylene \gg diisopropenyl. This variable activity is only conditioned by steric causes. The difference does not change with temperature, and decreases considerably if the polymerization reaction is carried out in a mixed solvent: hexane + diethyl ether. There are 3 figures, 1 table, and 4 references, 3 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR
(Institute of High Molecular Compounds of the Academy of Sciences, USSR)

SUBMITTED: February 5, 1959

Card 2/2

KOROTKOV, A.A.; LISHANSKIY, I.S.; SEMENOVA, L.S.

Catalytic polymerisation of olefins. Part 2: Effect of adding electron donors on the polymerisation of 1-pentene with the aid of complex catalysts. Vysokom.socd. 1 no.12:1821-1823 D '60.
(MIRA 13:5)

1. Institut vysokomolekulyarnykh soedineniy AN SSSR.
(Pentene) (Catalysts)

81581
S/190/63/002 '03/01/01;
B020/B066

5.2831

AUTHORS: Anosov, V. I., Korotkov, A. A.

TITLE: Low-temperature Copolymerization of Isobutylene With Diene
Hydrocarbon Admixtures in the Presence of Boron Trifluoride

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 3,
pp. 354-359

TEXT: The present paper describes the copolymerization of isobutylene with diene hydrocarbons in polar and non-polar solvents and in the presence of boron trifluoride. From the data obtained some conclusions are drawn as to the character of this reaction. The characteristics of the initial products and the performance of the copolymerization are described. The copolymerization experiments of isobutylene with diene hydrocarbons were carried out by a method described in a previous communication (Ref. 9). The solution of isobutylene, co-catalyst (isobutyl alcohol) and diene hydrocarbon in liquid ethylene or in a mixture of liquid ethylene and ethyl chloride, and the solution of boron trifluoride in ethylene were poured together into a glass vessel which

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Low-temperature Copolymerization of
Isobutylene With Diene Hydrocarbon Admixtures
in the Presence of Boron Trifluoride

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was dipped into a Dewar filled with ethylene. An equation is given for determining the mean viscosimetric molecular weight. Fig. 1 shows the dependence of the copolymerization intensity of isobutylene with diene hydrocarbons on the nature and concentration of the diolefin in an ethylene solution and in an ethylene - ethyl chloride mixture. Fig. 2 represents the dependence of the mean molecular weight of the copolymers on the nature and concentration of the diene hydrocarbons. Fig. 3 illustrates the dependence of the unsaturation of the copolymers on the nature and concentration of the diene hydrocarbons. The data obtained on the copolymerization of isobutylene with fluoroprene⁷ in a mixture of ethylene and ethyl chloride (1:1) in the presence of 0.03 mole/l boron trifluoride within a minute are tabulated. The main cause of the negative effect of the diene hydrocarbons on the copolymerization reaction with isobutylene in the presence of BF_3 is that the complexes formed at the end of the polymer chains, which contain diene hydrocarbon links, are less active and, therefore, favor a chain interruption. The reduced activity of the complexes is due to the fact that the positive

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Low-temperature Copolymerization of
Isobutylene With Diene Hydrocarbon Admixtures
in the Presence of Boron Trifluoride

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charge at the end of the polymer chain is weakened, because it is divided among at least three carbon atoms, and, in the case of halogen derivatives of diene hydrocarbons, halogen atoms additionally. The charge of the terminal carbon atom is not sufficient for the addition of the isobutylene molecule. The activity of the terminal complex with respect to the isobutylene addition will thus be changed in dependence on the nature of the hydrocarbon. The addition of diene hydrocarbons to the growing polymer chains, which contain isobutylene links at its end, also proceeds at different rates and depends on the hydrocarbon structure. An increase of the concentration of the diene hydrocarbon in the reaction mixture effects an increase of the rate of chain interruption, and the molecular weight of the copolymers drops. The diene hydrocarbons probably react more readily with BF_3 than isobutylene or the co-catalyst, thus forming stable complexes which are little active at low temperature and not able to initiate the copolymerization reaction. There are 3 figures, 1 table, and 13 references: 6 Soviet, 4 US, and 3 German. //

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Low-temperature Copolymerization of
Isobutylene With Diene Hydrocarbon Admixtures
in the Presence of Boron Trifluoride

S/190/60/002/03/01/014
B020/B066

ASSOCIATION: Yefremovskiy zavod sinteticheskogo kauchuka im. S. V.
Lebedeva (Yefremov Plant of Synthetic Rubber imeni S. V.
Lebedev)

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SUBMITTED: November 6, 1959

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KOROTKOV, A.A.

PART I BOOK REVISIONS 804/1983

International symposium on macromolecular chemistry. Moscow, 1960.

Nashimirovskiy simpozium po makromolekulyarnoy khimii, 80SR, Moskva, 14-18 Iyunya 1960 g; doklady i referenty. Sbornik II. International Symposium on Macromolecular Chemistry. Moscow, June 14-18, 1960. Papers and Summaries. Section II. [Moscow, Izdatel'stvo AN SSSR, 1960] 559 p. 5,500 copies printed.

Sponsoring Agency: The International Union of Pure and Applied Chemistry, Commission on Macromolecular Chemistry

Tech. Ed.: T.A. Prusakov.

PURPOSE: This book is intended for chemists interested in polymerization reactions and the synthesis of high-molecular compounds.

CONTENTS: This is Section II of a multivolume work containing papers on macromolecular chemistry. The papers in this volume treat mainly the kinetics of various polymerization reactions initiated by different catalysts or induced by radiation. Among the research techniques discussed are electron paramagnetic resonance spectroscopy and light-scattering interpolation. There are summaries in English, French and Russian. No personalities are mentioned. References follow each article.

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45

KOROTKOV, A. A., MITSCHENDLER, S. P. and KRASULINA, V. N. (USSR)

O kinetike i mekhanizme polimerizatsii metilmetakrylata butillitiem
On the kinetics and mechanism of methyl methacrylate polymerization
in the presence of lithium butyl
IUPAC S II:208-20

report presented at the Intl. Symposium on Macromolecular Chemistry, Moscow,
14-18 June 1960.

S/079/60/030/007/013/020
B001/B067

AUTHORS: Korotkov, A. A., Roguleva, L. F., Tsitokhtsev, V. A.

TITLE: Synthesis of 2-Tert.-butyl Butadiene-1,3[†]

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7,
pp. 2298 - 2303

TEXT: In the present paper, the condensation of olefins with aldehydes was used which had been successfully applied by other authors (Refs.4-6) for synthesizing the low dienes. Formaldehyde and 2,2,3-trimethyl-butene-3 (Ref. 1) which had been synthesized from pinacolone according to Ye. A. Favorskiy (Ref. 7) were used as initial products. This condensation in aqueous sulfuric acid gives compounds (II) and (III) whose total yield was 70% of the initial trimethyl butene (I) (Scheme 1). The dioxane (II) yield decreases with increasing temperature. The structure of compound (III) was quantitatively oxidized into the γ -lactone (IV) according to A. L. Pechnikov (Ref. 8) [abstracter's note: not into compound (V), as mentioned by Pechnikov]. The reduction of γ -lactone (IV) gives compound (VI), compound (II) forms compound (VII) in the

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Synthesis of 2-Tert.-butyl Butadiene-1,3

S/079/60/030/007/013/020
B001/B067

hydrolysis, with furan (III) being formed as a side product. The compounds (VI) and (VII) have the same empirical formula, they differ, however, by their physical properties, and give different derivatives with phenyl isocyanate (Scheme 2). The conversion of (II) into 2-tert.-butyl butadiene-1,3 (VIII) was made by catalytical pyrolysis over a phosphate catalyst at 385-400° in the presence of water vapors. The isomeric hydrocarbon (IX), the furan derivative (III), trimethyl butene (I), and the unchanged methyl-tert.-butyl dioxane (II) were formed as side products (Scheme 3). The compounds (VIII) and (IX) could not be separated by fractionation. The yield in (VIII) in the mixture was determined by forming the adduct with maleic acid aldehyde (75%). The following compounds were newly described: 4-tert.-butyl-4-methyl-dioxane-1,3; 2,2,3,3-tetramethyl-tetrahydrofuran; 3,3,4-trimethyl-pentane-1,4; 3,4,4-trimethyl-pentane-1,3, and 2,3,3-trimethyl-pentane-1,4. There are 10 references: 5 Soviet and 1 US. ✓C

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-molecular Compounds of the Academy of Sciences, USSR)

SUBMITTED: July 8, 1959

Card 2/2

5.3300

78291

SOV/79-30-3-45/69

AUTHORS: Korotkov, A. A., Lishanskiy, I. S., Fedorov, Ye. F.

TITLE: Synthesis of 2-Octylbuta-1,3-diene Using Organomagnesium Compounds

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 3, pp. 960-962 (USSR)

ABSTRACT: Preparation of 2-octylbuta-1,3-diene (III) by W. H. Carothers' method (W. H. Carothers, G. I. Berchet, J. Am. Chem. Soc., 55, 2813, (1933)) and reaction between 4-chlorobuta-1,2-diene (I) and octylmagnesium bromide (II) was studied. From a mixture obtained by the reaction of equimolar ether solutions of I and II, the following three fractions were separated. The first fraction: bp 28-30° (50 mm), n_D^{20} 1.4380, d_4^{20} 0.8438, colorless volatile liquid; apparently, it is $CH_2=C=CH-CH_2-CH_2-CH=CH_2$. The second fraction: bp 70-77° (5 mm), n_D^{20} 1.4522 (first run) and 1.4530 (last run), d_4^{20} 0.8924; this is 2-octylbuta-1,3-diene, obtained

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Synthesis of 2-Octylbuta-1,3-diene Using
Organomagnesium Compounds

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for the first time and characterized by its adduct with maleic anhydride. The third fraction: bp 109-110° (1.5 mm), hexadecane bp 110° (1 mm). The authors suggested that the reaction between I and II proceeds through the formation of an unstable intermediate complex, which rearranges into a stable cyclic complex. Decomposition of the latter leads to the formation of 4-alkylbuta-1,2-diene or 2-alkylbuta-1,3-diene. There are the following 4 U.S. references: W. H. Carothers, G. I. Berchet, J. Am. Chem. Soc., 55, 2813 (1933); W. H. Carothers, G. I. Berchet, J. Am. Chem. Soc., 55, 2807 (1933); J. H. Wotiz, J. S. Matthews, J. Am. Chem. Soc., 74, 2559 (1952); R. C. Fuson, H. D. Porter, J. Am. Chem. Soc., 70, 895 (1948).

ASSOCIATION: Institute of High Molecular Weight Compounds, Academy of Sciences USSR (Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR)

SUBMITTED: April 7, 1959
Card 2/2

S/190/60/002/012/009/019
B017/B055

AUTHORS: Korotkov, A. A., Mitsengendler, S. P., Aleyev, K. M.
TITLE: Effect of Diethyl Ether on the Copolymerization of Divinyl
and Styrene
PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 12,
pp. 1811-1816

TEXT: The influence of diethyl ether on the kinetics of the copolymerization of divinyl and styrene and the composition of the polymerizates formed were investigated. Fig. 1 shows the dependence of polymerizate composition on diethyl ether concentration. The experimental data on the copolymerization of divinyl and styrene in the presence of excess ether (4.8 mole/l) are listed in a table. Diethyl ether increases the activities of divinyl and styrene. In the presence of diethyl ether, the copolymerization of divinyl and styrene is very rapid. The effect of diethyl ether is explained by a decrease in the dissolving role of the divinyl monomer in the presence of complexing agents. Addition of 0.05 mole/l ether increases the styrene content of the copolymer from 13 to 25%.

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Effect of Diethyl Ether on the Copoly-
merization of Divinyl and Styrene

S/190/60/002/012/009/019
B017/B055

The maximum, 32%, is reached at 0.6 mole/l ether. With excess ether, the copolymerization constants were $\alpha_2 = 0.11$, $\beta_2 = 1.78$. The activity of the active centers solvated by ether varies therefore. The rate of divinyl polymerization in the presence of ether approaches that of styrene. There are 5 figures, 1 table, and 10 references: 4 Soviet, 5 US, and 1 Czechoslovakian.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR
(Institute of High-molecular Compounds of the Academy of
Sciences USSR)

SUBMITTED: May 20, 1960

Card 2/2

22561

S/190/61/003/005/004/014
B101/B218

5.1190

2209, 1274, 1257

AUTHORS: Korotkov, A. A., Li Tsung-ch'ang

TITLE: Influence of the structure of titanium trichloride on the stereospecificity of complex catalysts. II. Study of structural changes and of the catalytic properties of titanium trichloride during its thermal treatment

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 5, 1961, 691-698

TEXT: In a previous paper (Ref. 1: Vysokomolek. soyed., 3, 686, 1961) the authors established that the stereospecificity of the $\beta\text{-TiCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$ catalyst depends mainly on the structure of $\beta\text{-TiCl}_3$. The present paper reports on studies concerning the influence of thermal treatment upon the structure and catalytic properties of TiCl_3 . The preparation of $\beta\text{-TiCl}_3$ is described in Ref. 1. Thermal treatment was carried out in an evacuated ampoule (1-2 mm Hg) at constant temperature of an electric furnace (kept constant by an ЭПБ-01 (EPV-01) potentiometer), or a bath with Wood's alloy. The changes in the crystal structure of $\beta\text{-TiCl}_3$ due to heating were examined under an ЭМ-3 (EM-3) electron microscope, TiCl_3 being suspended in hexane

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S/190/61/003/005/004/014
B101/B218

Influence of ...

for the purpose. The cold crystals had a size of about $1-3 \mu$ and formed secondary formations of $3-10 \mu$ on heating. After 20-hr heating at 200°C , the latter were partially recrystallized to hexagonal prisms. At 400°C , the crystals grew bigger and adopted a more regular shape. Higher temperatures caused disproportionation of TiCl_3 to TiCl_2 and TiCl_4 . The determination of the specific surface of the samples by adsorption of nitrogen yielded results that agreed well with those found by electron-microscopic investigation. The change in the specific surface due to thermal treatment is shown in Table 1. X-ray pictures recorded by an ionization apparatus of the type $\text{NYP}-3$ (GUR-3) revealed a steady transition of the beta to the alpha modification at rising temperatures. The gamma modification described by G. Natta et al. (Ref. 2: Rend. Accad. Lincei, Cl. Sci. fis. mat. nat., 24, 121, 1958) could not be found. Alpha and beta phases were determined quantitatively by an 8-hr reaction with triethyl aluminum, subsequent centrifuging of the solid products, decomposing the latter by 2 N HCl, determining the content of H_2 proportional to Ti^{2+} in the gas liberated, and, finally, by means of the calibration curve of $\beta\text{-TiCl}_3$ (Fig. 6). Neither a molar ratio of Al/Ti between 1 and 4 nor protracted reaction (longer than 5hr) influenced the reduction of $\beta\text{-TiCl}_3$. This reaction is influenced, however, Card 2/8

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Influence of ...

by the concentration of $\text{Al}(\text{C}_2\text{H}_5)_3$ (Fig. 76) and by the temperature (Fig. 8).

The transition temperature which differs for each sample, varies between 250 and 350°C. At 200°C, the beta-to-alpha transition proceeds very slowly and takes more than 30 hr. At 20-25°C, propylene was polymerized with annealed TiCl_3 , $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ or $\text{Al}(\text{C}_2\text{H}_5)_3$. The molar ratio of the aluminum compounds and TiCl_3 was 2.5; the concentration of the former amounted to 0.05-0.1 mole/l. The stereoisomeric composition of the polymer was determined according to Ref. 1. The following results were obtained: With increasing beta-to-alpha conversion the content in the isotactic fraction of the polymer increases, while that of atactic and stereoblock fractions decreases. The authors therefore assume that the atactic fraction is caused by crystal defects of $\beta\text{-TiCl}_3$, and the isotactic fraction is due to a regular crystal structure of $\alpha\text{-TiCl}_3$. The catalytic activity of TiCl_3 does not change with increasing content of the alpha phase. Experiments with the system $\text{TiCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (Table 3) led to surprising results. In the presence of $\beta\text{-TiCl}_3$, this catalyst had a lower stereospecificity than the system $\alpha\text{-TiCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$, while its stereospecificity was higher in the

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presence of α - TiCl_3 . Furthermore, its stereospecificity remained unchanged even when TiCl_3 was heated to more than 500°C and contained 15% of TiCl_2 . Nevertheless, the activity of this catalyst was lower than that of the system with triethyl aluminum. The authors thank L. A. Volkova for X-ray pictures, B. S. Tuchkov for electron-microscopic studies, and S. P. Zhdanov for determining the specific surface. There are 8 figures, 3 tables, and 6 references: 4 Soviet-bloc and 5 non-Soviet-bloc.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute of High-molecular Compounds, AS USSR)

SUBMITTED: July 18, 1960

Card 4/8

KOROTKOV, A.A.; CHESNOKOVA, N.N.

Catalytic copolymerization of styrene and bivinyl. Vysokom.
soed. 2 no. 3:365-376 Mr '60. (MIRA 13:11)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo
kauchuka im.S.V.Lebedeva.

(Styrene) (Butadiene) (Polymerisation)

5.1190 1209 1274, 1297

22560
S/190/61/003/005/003/014
B101/B218

AUTHORS: Korotkov, A. A., Li Tsung-ch'ang

TITLE: Influence of the structure of titanium trichloride on the stereospecificity of complex catalysts. I. Influence of the conditions of manufacturing catalysts on the basis of β - TiCl_3 + $\text{Al}(\text{C}_2\text{H}_5)_3$ on their stereospecificity during propylene polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 5, 1961, 686-690

TEXT: The present paper deals with the influence exerted by the physical structure of TiCl_3 on the stereospecificity of the complex catalyst β - TiCl_3 + $\text{Al}(\text{C}_2\text{H}_5)_3$. TiCl_3 was obtained by reduction of TiCl_4 with diethyl aluminum chloride. The authors studied the polymerization of propylene obtained from propanol by dehydration with active Al_2O_3 . Polymerization took place in inert gas in two-piece ampoules. One part contained the titanium compounds, and the other $\text{Al}(\text{C}_2\text{H}_5)_3$ dissolved in heptane and

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X

Influence of ...

propylene. For some experiments, the components of the catalyst were mixed without the monomer. As may be seen from the experimental data given in Table 2, the temperature of β -TiCl₃ synthesis and the concentration of the components exerted only a small influence on stereospecificity. The sequence of mixing had a greater influence. Catalysts prepared at low temperatures were more active. TiCl₃ crystals obtained at low temperatures were fine-disperse and defective, and their radiogram was indistinct. The stereospecificity of the catalyst could be increased by a treatment of β -TiCl₃ with Al(C₂H₅)₃ solution at room temperature (Table 3). Such catalysts contained approximately 20% Ti²⁺. In the absence of the monomer, the mixing of the components had the same effect. The activity of the catalyst decreased. By substitution of Al(C₂H₅)₂Cl for Al(C₂H₅)₃, both stereospecificity and activity diminished. From the fact that no more than 50% of isotactic propylene polymer could be obtained with the help of β -TiCl₃ crystals, the authors conclude that the stereospecificity of the catalyst is due to the crystal structure of β -TiCl₃. β -TiCl₃ had a lower

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B101/3218

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stereospecificity than $\alpha\text{-TiCl}_3$. Degree of dispersion and defectiveness of the crystal are of minor influence. There are 1 figure, 3 tables and 8 non-Soviet-bloc references. The 2 most important references to English-language publications read as follows: G. Natta, J. Polymer Sci., 34, 23, 537, 1959; S. Murahashi, S. Nozakura, M. Sumi, Bull. Chem. Soc. Japan, 32, 1094, 1959.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute of High-molecular Compounds, AS USSR)

SUBMITTED: July 18, 1960

Table 2: Dependence of the stereospecificity of the catalyst on the conditions of $\beta\text{-TiCl}_3$ synthesis (conditions of polymerization: 20-25°C;

$\text{Al}(\text{C}_2\text{H}_5)_3/\text{TiCl}_3 = 2-2.5$; solvent: heptane¹).

Legend: a) conditions of synthesis; b) number of samples; c) reaction temperature; d) concentration of initial reagents (mole/l); e) duration of polymerization, hr; f) yield of solid polymer; g) extraction; h) ethereal extract; i) n-heptane extract; k) residue. Annotations: ¹) As a rule, Card 3/5

MITSENGENDLER, S.P.; IVANOV, N.N.; KOROTKOV, A.A.

Effect of the nature of the medium and catalyst on catalytic
polymerization. *Vysokom. soed.* 3 no.2:219 F '61. (MIRA 14:5)
(Polymerization) (Catalysts)

KOROTKOV, A.A.; RAKOVA, G.V.

Copolymerization of isoprene and styrene in the presence
of butyllithium. Vysokom.soed. 3 no.10:1482-1490 0 '61.
(MIRA 14:9)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR.
(Isoprene) (Styrene) (Polymerization)

15.8060

20907
S/190/61/003/012/001/012
B101/B110

AUTHORS: Pozamantir, A. G., Korotkov, A. A., Lishanskiy, I. S.
TITLE: Catalytic polymerization of olefins. III. Effect of the composition of the Ziegler catalyst on the molecular weight of polyethylene
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 12, 1961, 1769 - 1773

TEXT: The authors discuss various publications on the relationship between the composition of the Ziegler catalyst and the molecular weight of the polymer. In a former paper (Ref. 6: A. G. Pozamantir, Vysokomolek. soyed., 2, 1026, 1960), it was shown that some halogen derivatives of hydrocarbons and SnCl_4 tear off the reaction chain and decrease the molecular weight of polyethylene. In the present study, it was investigated whether TiCl_4 had a similar effect as SnCl_4 . The dependence of the molecular weight on the composition of the catalysts on the basis of aluminum alkyls, TiCl_3 , and TiCl_4 , was investigated experimentally. The

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B101/B110

Catalytic polymerization of...

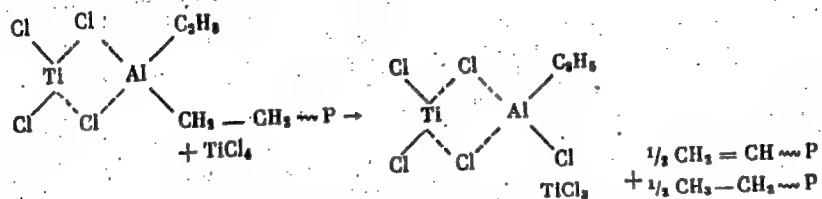
synthesis of organoaluminum compounds had been described earlier (Vysokomolek. soyed., 1, 1207, 1959). Polymerization of C_2H_4 was achieved, according to Ref. 6, at $50^\circ C$. The concentration of $TiCl_4$ was $4.4 \cdot 10^{-3}$ moles/liter; that of $TiCl_3$, $8.2 \cdot 10^{-3}$ moles/liter. At first $TiCl_3$, later the aluminum alkyl, were added to the reaction mixture. In the tests with $TiCl_4$, this compound was added last. The intrinsic viscosity of the polymer was determined in decalin at $135^\circ C$. Polymerization of C_2H_4 by means of catalysts on the basis of $(C_2H_5)_3Al$; $(C_2H_5)_2AlCl$; or $C_2H_5AlCl_2$, and $TiCl_3$, $TiCl_4$, led to the results indicated in Fig. 1. Experiments in which $TiCl_4$ was added in increasing amounts to an aluminum alkyl + $TiCl_3$ catalyst resulted in decreasing molecular weight with increasing ratio $TiCl_4/TiCl_3$. The following conclusions were drawn: (1) The molecular weight of the polymer depends on the concentration of $TiCl_4$ which did not react. The concentration of $TiCl_4$ depends on the reactivity of the

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B101/B110

Catalytic polymerization of...

aluminum alkyl and on the ratio Al/Ti. (2) TiCl_4 tears off the reaction chain. The growing chain of the polymer is expelled from the active center by a chlorine atom of TiCl_4



A study by Ye. P. Tepenitsina, M. I. Farberov et al. (Vysokomolek. soyed., 1, 1148, 1959) is mentioned. There are 2 figures and 13 references: 3 Soviet and 10 non-Soviet. The four most recent references to English-language publications read as follows: N. G. Gaylord, H. F. Mark, Linear and Stereoregular Addition Polymers, Intersci. Publ. Inc., N. Y., 1959, p. 122; R. van Helden, A. F. Bickel, E. C. Kooyman, Tetrahedron Letters, 12, 18, 1959; L. Rodriguez, J. Gabant, B. Hargitay, Tetrahedron Letters, 17, 7, 1959; K. Ziegler, H. Martin, J. Stedefeder, Tetrahedron Letters, Card 3/4

Catalytic polymerization of...

20, 12, 1959.

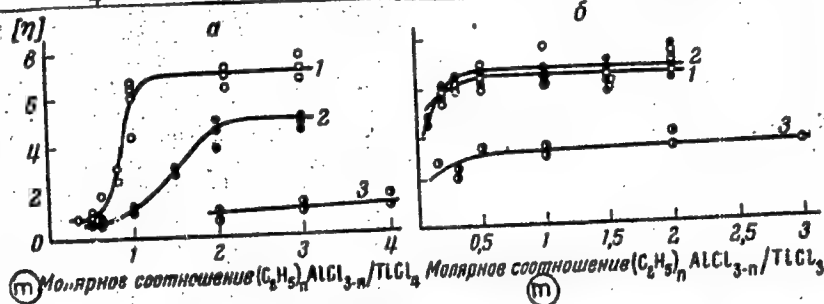
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B101/B110

ASSOCIATION: Okhtinskiy khimicheskiy kombinat (Okhta Chemical Combine).
Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute
of High-molecular Compounds AS USSR)

SUBMITTED: December 23, 1960

Fig. 1. Dependence of the molecular weight of polyethylene on ratio:
(a) aluminum alkyl : TiCl_4 ; (b) aluminum alkyl : TiCl_3 . (1) $(\text{C}_2\text{H}_5)_3\text{Al}$;

(2) $(\text{C}_2\text{H}_5)_2\text{AlCl}$; (3) $\text{C}_2\text{H}_5\text{AlCl}_2$;
(m) molar ratio;
temperature = 50°C ;
concentration of
 $\text{TiCl}_4 = 2.2 \cdot 10^{-3}$
moles, of TiCl_3
 $= 4.1 \cdot 10^{-3}$ moles in
500 ml of benzene.



S/190/62/004/001/020/020
B106/B110

AUTHORS: Korotkov, A. A., Artamonova, I. L.
TITLE: Reaction of titanium tetrachloride with butyl lithium
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 1, 1962, 145

TEXT: M. H. Jones and collaborators (Ref. 2; see below) found that the reduction of titanium tetrachloride with butyl lithium did not proceed quantitatively, even with high excess of the latter; hence, they concluded that butyl lithium was a poor reducing agent. Contrary to these statements, the authors found butyl lithium to be a good reducing agent for titanium tetrachloride. The reaction flask was heated in vacuum to 250°C before the reaction, and dry argon was passed through. A brown precipitate was formed when conducting the reduction at 25°C by vigorous mixing and adding butyl lithium dropwise to a solution of titanium tetrachloride in hexane. Within 15 min, the tetravalent titanium was more or less quantitatively reduced to the trivalent stage when the reactants were in equimolar ratio. If the reaction took place under equal conditions but in reverse order of

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38275

S/196/62/004/006/001/026
B.O./3110

5.3830

15.9201

AUTHORS: Keretkov, A. A., Marandzheva, Ye. N.

TITLE: Thermochemical study of the catalytic polymerization of isoprene. II. Effect of temperature on the overall heat effect of the polymerization of isoprene with butyl lithium

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 6, 1962, 793-802

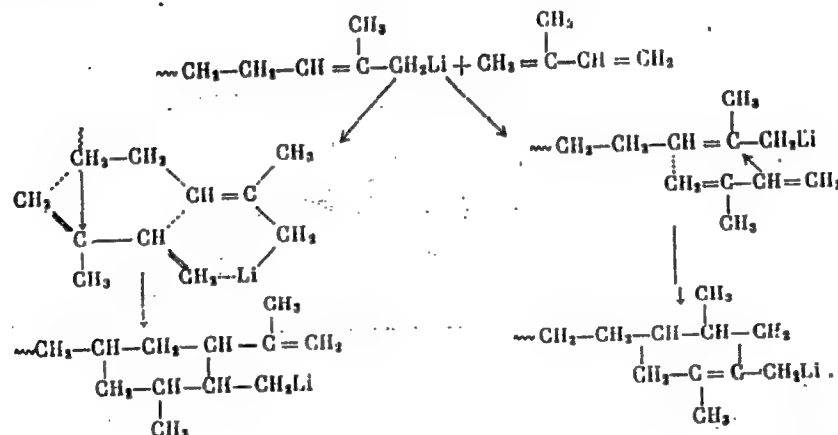
TEXT: The polymerization of isoprene dissolved in benzene with butyl lithium was studied with a view to a qualitative appreciation of the side reactions. The overall heat effect, Q_s , of the polymerization was measured calorimetrically at 35°C with diethyl ether as calorimeter liquid, at 42°C with methylal, at 51°C with acetone + hexane, at 61.3°C with chloroform, at 80.2°C with benzene, and at 87.7°C with propanol + water. According to Kirchhoff's rule, an increase of the polymerization temperature by 50°C should raise the heat effect by 350-400 cal/mole only; but here an increase of more than 3000 cal/mole was observed: 15.7 kcal/mole at 42°C, 19 kcal/mole at 87.7°C. A discussion of this

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S/190/62/004/006/001/026
B101/B110

Thermochemical study of the ...

effect reveals that it cannot be caused by cross linking, since ΔQ is independent both of the concentration of monomer and catalyst and of the degree of polymerization. An intramolecular ring formation is therefore assumed:



Card 2/3

Thermochemical study of the ...

S/190/62/004/006/001/026
B101/B110

This reaction also corresponds to the observed decrease of insaturation from ~100% at 35°C to ~88% at 87.7°C. $\Delta Q = Q_2 k_5 / k_2$ (Q_2 = heat effect of ring formation, k_5 = reaction constant of ring formation, k_2 = reaction constant of polymerization). If the constants of the Arrhenius equation are substituted for k_2 and k_5 , a linear function $\log \Delta Q = f(1/T)$ is obtained in agreement with the experiment. The activation energy of the ring formation is 34 ± 4 kcal/mole, the factor A of the Arrhenius equation being $2.3 \cdot 10^{22} \pm 10^3$. This ring formation does not occur in free radical polymerization of bis-ethylene hydrocarbons. There are 5 figures and 1 table.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka (All-Union Scientific Research Institute of Synthetic Rubber)

SUBMITTED: July 15, 1960

Card 3/3

38281

U/190/52/004/006/007/025

B110/0138

15.2070

AUTHORS: Azimov, A. A., Mitsengendler, S. P., Korotkov, A. A.

TITLE: synthesis and investigation of the structure of catalytic poly-n-butyl methacrylate. I. Synthesis of poly-n-butyl methacrylate of stereoregular structure

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 6, 1962, 835-838

TEXT: Stereoisomeric poly-n-butyl methacrylates (PBMA) were synthesized. n-butyl methacrylate was purified by alkali, rinsed with water, dried with $MgSO_4$ and KH , distilled and polymerized in toluene, hexane, diethyl ether, liquid ammonia or tetrahydrofuran by means of butyl lithium. Investigated were: (1) optical anisotropy of the solutions and the photoelastic effect, (2) dielectric losses, dipole moments and densities, (3) nuclear magnetic resonance and the IR spectra. Polymerization in toluene at $-50^{\circ}C$ with butyl lithium (concentration: 1.0 and 0.004-0.005 mole/liter) produced a molecular weight of $6 \cdot 10^6$ at 90% depth of polymerization. The molecular

Card 1/3

Synthesis and investigation of the ...

S/190/62/004/006/007/026
B110/B138

weights increase with depth of polymerization. Since the ratio of the rate constants, k_2/k_1 , is ten times higher for butyl methacrylate than for methyl methacrylate, higher molecular weights were obtained. The polymer formed in hexane is partly separated as a fine precipitate. The polymers obtained in toluene, hexane and diethyl ether have identical structure and differ from the polymers obtained by means of Li metal and α -sodium naphthalene, and liquid ammonia and tetrahydrofuran. The nuclear magnetic resonance spectra showed isotactic structure for the first polymers, and syndiotactic for the second polymers. For the first group, between $1900-600\text{ cm}^{-1}$, fewer absorption bands exist in the IR spectra. The vitrification temperature of the first group was -15 to -14°C , that of the second one $30-33^\circ\text{C}$. For the first group, the optical anisotropy was $\alpha = -2$, for the second $\alpha = -14$. Densities differed only slightly ($1.06-1.07$). The mechanism of isotactic and syndiotactic PBMA formation appears to be similar to that of polymethyl methacrylate. There is 1 table.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR
(Institute of High Molecular Compounds AS USSR)

Card 2/3

Synthesis and investigation of the ...

S/190/62/004/006/007/026
B110/B130

SUBMITTED: April 6, 1961

Card 5/5

S/020/61/141/003/008/021
B103/B101

AUTHORS: Petrov, G. N., and Korotkov, A. A., Corresponding Member
AS USSR

TITLE: Study of the composition of the reaction products of
vanadium oxytrichloride with triethyl aluminum

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 141, no. 3, 1961, 632-635

TEXT: The work presented was undertaken with a view to establishing rules which enable an advance calculation of the quantitative composition of the reaction products obtained from VOCl_3 and $\text{Al}(\text{C}_2\text{H}_5)_3$. 0.1 M benzenic solution of $\text{Al}(\text{C}_2\text{H}_5)_3$ was added to 0.1 M VOCl_3 solution at 20°C under strict exclusion of moisture oxygen. The test series carried out were: (I) The precipitate was filtered off, washed several times with benzene and dissolved in 2% H_2SO_4 . The mean valency of V was determined volumetrically with 0.1 N permanganate solution. Then the precipitate and the filtrate were analyzed quantitatively for Cl, Al, and V. (II) The ethane, ethylene, and butane evolved was collected and burned. The Card 1/5

Study of the composition ...

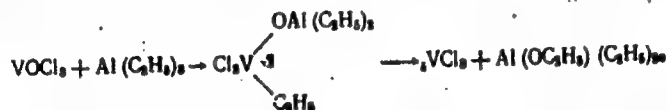
S/020/61/141/003/008/021
B103/B101

quantity of CO_2 formed was used as a basis for determining the amount of ethyl groups of $\text{Al}(\text{C}_2\text{H}_5)_3$ which had react under formation of hydrocarbon gases. According to Ref. 9 (see below) it was assumed that the instable organovanadium intermediate compounds decompose practically quantitatively, and that the polymerization of ethylene is negligible. In this case the quantity of reacted ethyl groups is equivalent to the amount of $\text{AlCl}(\text{C}_2\text{H}_5)_2$ formed. After removing the hydrocarbon gases, the reaction mixture was treated with 2% H_2SO_4 and the amount of unreacted ethyl groups calculated from the quantity of ethane evolved. From these data, the quantities of $\text{Al}(\text{OC}_2\text{H}_5)(\text{C}_2\text{H}_5)_2$ and unreacted $\text{Al}(\text{C}_2\text{H}_5)_3$ were calculated. It was found that the mean valency of V decreases with increasing molar ratio $[\text{Al}(\text{C}_2\text{H}_5)_3]/[\text{VOCl}_3] = n$ in the range $n < 2$ (Fig. 1). The quantity of $\text{AlCl}(\text{C}_2\text{H}_5)_2$ formed increases simultaneously. At $n \geq 2$ the valency of V becomes constant. V, therefore, reacts simultaneously along two different paths: (1) at the V - Cl bond (according to Ref. 10, see below):
Card 2/05

S/020/61/141/003/008/021
B103/B101

Study of the composition ...

$\text{VOCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_3 \rightarrow \text{C}_2\text{H}_5\text{VOCl}_2 + \text{AlCl}(\text{C}_2\text{H}_5)_2$; $\text{C}_2\text{H}_5\text{VOCl}_2 \rightarrow \text{VOCl}_2 + \text{Et}$, where Et are the ethyl groups determined as gaseous hydrocarbons; (2) at the V = O bond:

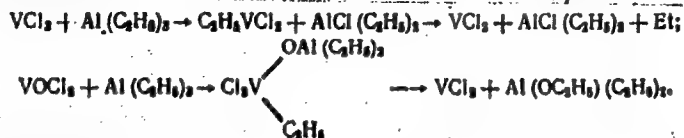


Thus the valency of V drops by one unit due to the formation of 1 mole $\text{AlCl}(\text{C}_2\text{H}_5)_2$, and by 2 units due to the formation of $\text{Al}(\text{OC}_2\text{H}_5)(\text{C}_2\text{H}_5)_2$. The mean values of the V valency, calculated for both reactions are in good agreement. The present paper describes the simplest system formed at $n > 2$. The insoluble complex compounds formed during the reduction are composed of equimolar amounts of vanadium chlorides and alkyl aluminum compounds, which are able to undergo an equilibrium exchange with the alkyl aluminum in solution. At $n > 2$, the Cl content of the solution above the precipitate increases. With excess $\text{Al}(\text{C}_2\text{H}_5)_3$, the trivalent and tetravalent V compounds formed are further reduced.

Card 3/4 5

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B103/B101

Study of the composition ...



Since no further reduction of V occurs, this Cl increase is probably due to an equilibrium:

$\text{VCl}_2 \cdot \text{AlCl}(\text{C}_2\text{H}_5)_2 + \text{Al}(\text{C}_2\text{H}_5)_3 \rightleftharpoons \text{VCl}_2 \cdot \text{Al}(\text{C}_2\text{H}_5)_3 + \text{AlCl}(\text{C}_2\text{H}_5)_2$. A similar reaction is assumed for $\text{Al}(\text{OC}_2\text{H}_5)(\text{C}_2\text{H}_5)_2$. The following designations are used: m_0 - total content of $\text{AlCl}(\text{C}_2\text{H}_5)_2$; l_0 - total content of

$\text{Al}(\text{OC}_2\text{H}_5)(\text{C}_2\text{H}_5)_2$ in the reaction products; m and l , respectively, the content of these compounds in the solution; m_1 and l_1 the quantities of these compounds which are chemisorbed by the surface of the precipitate. It is assumed that $m_0 = m + m_1$; and $l_0 = l + l_1$. From the results obtained and the equation of the equilibrium constants of the respective reactions the following equations are derived: $m_1 = m_0/n$, $l_1 = l_0/n$. Thus the quantity of $\text{AlCl}(\text{C}_2\text{H}_5)_2$ chemisorbed by the surface of the reduced vanadium

Card 4/8 5

S/190/62/004/009/009/014
B101/B144

AUTHORS: Mitsengendler, S. P., Andreyeva, G. A., Sokolova, K. I.,
Korotkov, A. A.

TITLE: Synthesis of graft copolymers by the action of polymeric
organometallic compounds on polar polymers, and study of
their properties. I. Synthesis of graft copolymers of
styrene and methyl methacrylate

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 9, 1962, 1366-1374

TEXT: The interaction of polystyrene lithium (PS⁺) with polymethyl
methacrylate (PMMA) was studied. The decomposition of PS⁺ by moisture
and oxygen was eliminated by treating it in vacuo or in a nitrogen
atmosphere, and through the presence of methyl lithium or calcium hydride.
PMMA dissolved in toluene was cooled to -50 - -70°C and mixed with PS⁺
cooled to -78°C. The resulting graft copolymer was extracted successively
with ether, acetonitrile and benzene. The ratio >C=O/PS^+ was determined
from the oxygen content of the graft copolymer or by IR-spectroscopy.
Results: (1) All fractions differed from a mechanical mixture of the

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Synthesis of graft copolymers...

S/190/62/004/009/009/014
B101/B144

components by birefringence. A graft copolymer was obtained with 100% yield. (2) The molecular weight and the ratio of components affect the reaction course; (a) An increasing molecular weight of PMMA reduces the selectivity and renders grafting of PS* onto the macromolecule of PMMA uniform. If the molecular weight of PMMA is increased from $70 \cdot 10^3$ to $500 \cdot 10^3$, and if the ratio $\Delta C=O/PS^*$ equals 10, the amount of PMMA consumed for ether fraction decreases from 31 to 3.6%, and the yield of ether fraction from 74 to 18.6%; (b) an increasing molecular weight of PS* increases the selectivity and reduces the uniformity of grafting. If the molecular weight of PS* increases from $5 \cdot 10^3$ to $50 \cdot 10^3$, the PMMA consumption for ether fraction rises from 3.1 to 53% and the yield of this fraction from 20.5 to 95.5%; (c) if the molecular weights of PMMA and PS* are constant, the yield of ether fraction increases as the concentration of PS* is increased, or as the ratio $\Delta C=O/PS^*$ is decreased. Conclusions: The occurrence of grafting is not statistical but mainly on that PMMA macromolecule where the reaction has already started. As soon as grafting of the first PS* chains sets in, the coiled PMMA molecules begin to stretch and thereby to facilitate further grafting. High molecular

Card 2/3

Synthesis of graft copolymers...

S/190/62/004/009/009/014
B101/B144

weight or concentration of PS* support this effect. By suitably choosing the molecular weight and the ratio of the components it is possible to synthesize copolymers with the desired composition and branching. There are 4 figures and 3 tables.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute of High-molecular Compounds AS USSR)

SUBMITTED: May 29, 1961

Card 3/3

S/190/63/005/002/009/024
B101/B102

AUTHORS: Mitsengendler, S. P., Alejev, K. M., Dantsig, L. L.,
Korotkov, A. A.

TITLE: Effect of the nature of the ether on styrene-divinyl
copolymerization using butyl lithium

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 2, 1963,
212-216

TEXT: Since it has been found previously (Vysokomolek. soyed., 2, 1811, 1960) that addition of diethyl ether accelerates the copolymerization of styrene (St) and divinyl (DV) and influences the composition of the copolymer, copolymerization of equimolecular parts of St and DV was performed in benzene at 30°C with 0.05 mole/l butyl lithium in the presence of different ethers. Results;

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Effect of the nature of the ...

9/190/63/005/002/009/024
B101/B102

ether	concentration mole/l	composition of the copolymer, %	
		St	DV
-	-	13.6	86.4
diethyl ether	1.1	30.8	69.2
dioxane	1.1	30.0	70.0
methylal	1.1	30.6	69.4
tetrahydrofuran	1.1	45.9	54.1
tetrahydrofuran	3.0	48.4	51.6
ethylene glycol dimethyl ether	1.1	47.8	52.2

The copolymerization constants α (St) and β (DV) were:

	α	β
without ether	0.05	20
with diethyl ether	0.11	1.74
with tetrahydrofuran	0.744	1.030

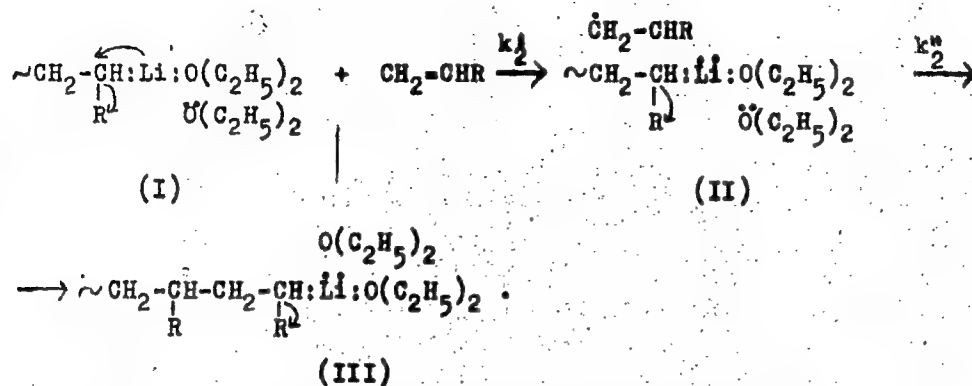
The polymerization rate in the presence of tetrahydrofuran was 5-6 times higher than in the presence of

diethyl ether and 100 times higher than without ether. This is explained by complex formation, taking diethyl ether as example:

Card 2/4

Effect of the nature of the ...

S/190/63/005/002/009/024
B101/B102



The highly active ethers, such as tetrahydrofuran and ethylene glycol dimethyl ether, form stable complexes with a highly polar C-Li bond owing to slight steric hindrance and the isomerization of complex II to complex III proceeds rapidly, the structure of the components having only a small effect so that $\alpha \sim \beta$. With diethyl ether, dioxane, and methylal, the rate

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MITSENGENDLER, S.P.; ANDREYEVA, G.A.; SOKOLOVA, K.I.; KOROTKOV, A.A.

Synthesis of graft copolymers by the action of polymeric organometallic compounds on polar polymers and a study of their properties. Part 1: Synthesis of graft copolymers of styrene and methyl methacrylate. Vysokom.sped. 4 no.9:1366-1374 S '62. (MIRA 15:11)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR.
(Styrene)
(Methacrylic acid) (Polymerization)

KOZLOV, P.V., otv. red.; ANDRIANOV, K.A., red.; DOGADKIN, B.A., red.;
DOLGOPLOSK, V.A., red.; YENIKOLOPYAN, N.S., red.; KARGIN,
V.A., red.; KOLESNIKOV, G.S., red.; KOROTKOV, A.A., red.;
KORSHAK, V.V., red.; LAZURKIN, Yu.S., red.; MEDVEDEV, S.S.,
red.; MIKHAYLOV, N.V., red.; PASYNSKIY, A.G., red.;
SLONIMSKIY, G.L., red.; SMIRNOV, V.S., red.; TSVETKOV, V.N.,
red.; FREYMAN-KRUPENSKIY, D.A., tekhn. red.

[Adhesion of polymers] Adgeziia polimerov; sbornik statei.
Moskva, Izd-vo AN SSSR, 1963. 142 p. (MIRA 16:10)
(Polymers) (Adhesion)

MITSENGENDLER, S.P.; ALEYEV, K.M.; DANTSIG, L.L.; KOROTKOV, A.A.

Effect of the nature of ether on the copolymerization of styrene
and bivinyl by butyllithium, *Vysokom.soad.* 5 no,2:212-216 P '63,
(MIRA 16:2)

1, Institut vysokomolekulyarnykh soyedineniy AN SSSR.
(Ethers) (Polymerization) (Styrene)
(Butadiene)

KOLESNIKOV, G.S., otv. red.; ANDRIANOV, K.A., red.; DOGADKIN, B.A., red.; DOLGOPLOSK, B.A., red.; YENIKOLOPYAN, N.S., red.; KARGIN, V.A., red.; KOZLOV, P.V., red.; KOROTKOV, A.A., red.; KORSHAK, V.V., red.; LAZURKIN, Yu.S., red.; MEDVEDEV, S.S., red.; MIKHAYLOV, N.V., red.; PASYNSKIY, A.G., red.; SLONIMSKIY, G.L., red.; SMIRNOV, V.S., red.; TSVETKOV, V.N., red.; FREYMAN-KRUPENSKIY, K.A., tekhn. red.

[Carbochain high-molecular weight compounds] Karbotsepye vysokomolekuliarnye soedineniia; sbornik statei. Moskva, Izd-vo AN SSSR, 1963. 287 p. (MIRA 17:1)

AZIMOV, Z.A.; KOROTKOV, A.A.; MITSENGENDLER, S.P.

Kinetics and mechanism of n-butyl methacrylate polymerization
under conditions of isotactic polymer formation. Vysokom.soed.
5 no.8:1144-1151 Ag '63. (MIRA 16:9)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR.
(Methacrylic acid) (Polymerization)

KOROTKOV, A.

Synthetic rubber will replace the natural. Nauka i zhyttia 12
no.3:8 Mr '63. (MIRA 16:11)

1. Chlen-korrespondent AN SSSR

KOLESNIKOV, G.S., otv. red.; ANDRIANOV, K.A., red.; DOGADKIN, B.A., red.; DOLGOPLOSK, B.A., red.; YENIKOLOPYAN, N.S., red.; KARGIN, V.A., red.; KOZLOV, P.V., red.; KOROTKOV, A.A., red.; KORSHAK, V.V., red.; LAZURKIN, Yu.S., red.; MEDVEDEV, S.S., red.; MIKHAYLOV, N.V., red.; PASYNSKIY, A.G., red.; SLONIMSKIY, G.L., red.; SMIRNOV, V.S., red.; TSVETKOV, V.N., red.; FREYMAN-KRUPENSKIY, D.A., tekhn. red.

[Heterochain high-molecular weight compounds] Geterotsepnnye vysokomolekuliarnye soedineniia; sbornik statei. Moskva, Izd-vo "Nauka," 1963. 246 p. (MIRA 17:3)

ACCESSION NR: AP4010039

S/0062/64/000/001/0055/0061

AUTHOR: Azimov, A. A.; Korotkov, A. A.; Mitsengendler, S. P.

TITLE: Kinetics and mechanism of polymerizing tert.-butylmethacrylate with n-butyllithium.

SOURCE: AN SSSR. Izvestiya. Ser. khim., no. 1, 1964, 55-61

TOPIC TAGS: tert.butylmethacrylate polymerization, methylmethacrylate polymerization, n.butylmethacrylate polymerization, polymerization kinetics, polymerization mechanism, n.butyllithium, homogeneous polymerization, reaction constant, activation energy, polymerization center formation, chain growth, chain termination, catalyst destruction, reaction rate, alkylmethacrylate, polymerization

ABSTRACT: The kinetics and polymerization mechanism of homogeneous polymerization of tert.-butylmethacrylate (t-BMA) in toluene at -50C to -70C in wide ranges of monomer and catalyst concentrations were studied. The appar-

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ACCESSION NR: AP4010039

ent constants, the activation energy and the pre-exponents of the elemental reactions (formation of polymerization centers, chain growth and termination, and destruction of catalyst) were calculated. Values for t-BMA were compared with those for methylmethacrylate (MMA) and n-butylmethacrylate (n-BMA). The high values for the pre-exponents in the Arrhenius equation for t-BMA (in the 10^{13} range as compared to 10^3 and 10^5 for MMA and n-BMA) determined the notably high apparent constants of the elemental reactions. The complex compounds formed as intermediates in the elemental reactions are less stable than those of MMA and n-BMA. The ratio of the constants for the reaction of forming active centers to the chain growth reaction is higher for the t-BMA; the polymerization proceeds without an induction period and the product polymers have a lower molecular weight than those of MMA and n-BMA. In polymerizing alkylmethacrylates 0.5%-6% of the n-butyllithium is spent on the reaction of forming active centers; the main portion is spent on reaction with the C=O bond. Orig. art. has: 7 figures, 3 tables and 6 equations.

ASSOCIATION: Institut vy*sokomolekulyarniy*kh soyedineniy Akademii nauk

Card 2/3

ACCESSION NR: AP 4010039

SSSR (Institute of High Molecular Compounds, Academy of Science SSSR)

SUBMITTED: 01Apr63

DATE ACQ: 14Feb64

ENCL: 00

SUB CODE: CH, PH

NO REF SOV: 008

OTHER: 003

Card 3/3

ACCESSION Nr. AP4022958

B/0020/64/155/001/0136/0138

AUTHOR: Korotkov, A. A. (Corresponding member); Lishanskiy, I. S.; Zak, A. G.

TITLE: Polymerization of pentene-1 in the presence of isoprene on a complex catalyst

SOURCE: AN SSSR. Doklady*, v. 155, no. 1, 1964, 136-138

TOPIC TAGS: polymerization, Ziegler catalyst, pentene 1, isoprene, polyisoprene, polypentene, refractive index, chain termination, pentene isoprene, homopolymer mixture, copolymerization, catalyst component ratio, catalyst active center

ABSTRACT: The copolymerization of olefins with dienes, specifically of pentene-1 with isoprene, with a Ziegler catalyst was investigated. The catalyst was prepared by the interaction of various amounts of $TiCl_3$ with $Al(iso-butyl)$ to form products with Al:Ti ratios from 1.0:1.0 to 2.0:1.0. With almost equal proportions of Al and Ti, isoprene polymerizes in high yield (about 90%) to form high molecular cis-1,4-polyisoprene; with Al:Ti = 2:1, the yield drops to 1.5%. The yield of pentene-1 polymer is low (5.5-11.5%) regardless of the catalyst component ratio. On polymerizing a mixture of monomers with Al:Ti = 1:1, the product polymer (a mixture of homopolymers) contains 83% isoprene; the yield and viscosity are lower

Cord 178

ACCESSION NR: AP4022958

than for isoprene alone. The Al:Ti=1:1 catalyst is described as apparently having two types of active centers, one specific for isoprene and the second for pentene-1. When the Al component ratio is higher, the second type of active center is apparently completely disintegrated while the first is only partially disintegrated. A third type of active center, specific for pentene-1 is formed simultaneously, but is almost completely blocked because of strong adsorption of isoprene. Therefore polymerization of pentene-1 is almost impossible even with Al:Ti = 1.8:1 to 2:1. When isoprene is polymerized in the presence of pentene-1, isoprene chain termination is effected with an Al:Ti ratio above 1.2:1. The refractive indices of films of the polymers and copolymerization products were found additive, with n_D^{20} of polypentene = 1.4800 and of polyisoprene = 1.5218. (fig.) Orig. art. has: 1 figure and 3 tables.

ASSOCIATION: Institut vy'sokomolekulyarny'kh soyedineniy AN SSSR (Institute of high-molecular compounds, AN SSSR)

SUBMITTED: 20Sep63

DATE ACQ: 08Apr64

ENCL: 01

SUB CODE: CH

NO.REF. SOV: 003

OTHER: 004

Card 2/82

011111022 ENI(M)/EPH(C)/EWP(J)/T Fc-4/Pr-4 GS/A; 00

AT5019601

001/0013

Protkov, A. A.; Kormer, V. A.; Krupyshev, M. A.; Ierlinger, D. P.

Synthesis of isoprene rubber

Resoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka.

TOPIC TAGS: synthetic rubber, isoprene, polymerization, Ziegler catalyst, organo-metallic complex

ABSTRACT: Polymerization of isoprene was studied with Ziegler-type and organometallic- π -complex catalysts in order to simulate the natural rubber. Production of commercial synthetic SKI-3 rubber is based on the results of this study. In general, the Ziegler-type catalyst [TiCl_4 reduced with $\text{Al}(\text{C}_2\text{H}_5)_3$] gave isoprene polymers containing up to 95% of cis-1,4 units, while the organo- π -complexes of Li, Zn, and Al gave polymers with varying ratio of cis-1,4 to cis-3,4 and trans-1,4 units. The higher the cis-1,4 unit content in the polymer the better the mechanical properties of the vulcanized product. In the case of the Ziegler catalyst, the experiments

Card 1/2

101198-5

ACCESSION NR: AT5019601

were conducted at -30° to 100°C using a 1:1 and 1:2 mixture of TiCl_4 and $(\text{iso-C}_4\text{H}_9)_3\text{Al}$ as catalyst. The initial isoprene concentration was 15-50 wt. %, the catalyst concentration was 2.2-3.6 wt. % based on monomer, and the polymerization duration was 1-10 hours. A mixture of isopentenes, isoprene, isopentadiene, trimethyl methyl ethylene were used as monomers. The reaction was carried out in the presence of a solvent (prior to the polymerization) and the highest strength and relative elongation were obtained in the highest strength and relative elongation). Polymers prepared at 50°C have the best mechanical properties. Unsaturated hydrocarbon solvents gave lower rates of isoprene polymerization than the saturated hydrocarbon solvents. The rate of polymerization reaction is reduced and the polymer quality is impaired when there is no solvent. Orig. art. has: 8 tables and 2 figures.

ASSOCIATION: none

SUBMITTED: 24Oct64

ENCL: 00

SUB CODE: MT, CC

NUMBER: 006

OTHER: 003

Page 2/2

L 60199-65 EWT(m)/EPF(c)/EWG(m)/EWP(j)/T PC-4/PT-4 DS/WW/RS/JAJ/RM

ACCESSION NR: AT5019602

UR/000

000/0014/0040

AUTHOR: Korotkov, A. A.; Chasnokova, N. N.; Krupyshev, M. A.

33
341

TITLE: Mechanism and kinetics of catalytic polymerization of isoprene

SOURCE: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka. Katalizatsiya izoprena kompleksnymi katalizatorami (Catalysis of Isoprene by complex catalysts). Moscow, Izd-vo Khimiya, 1964, 14--v

TOPIC TAGS: isoprene polymerization, kinetics, mechanism, catalyst, catalysis

ABSTRACT: Effect of temperature and concentrations of monomer and catalyst on kinetics of isoprene polymerization in isopentane and on polymer molecular weight and microstructure was studied at 10°, 20°, and 30°C. $TiCl_3$ activated with $(iso-C_4H_9)_2AlCl$ served as catalyst. Experiments were also conducted without a solvent in benzene solution. The initial rate of polymerization up to 25% conversion is described by the equation:

$$W \propto \frac{a \cdot k_1 \cdot k_2 \cdot m_0^2}{k_3} \left(n_0 - \frac{1}{K} \right)$$

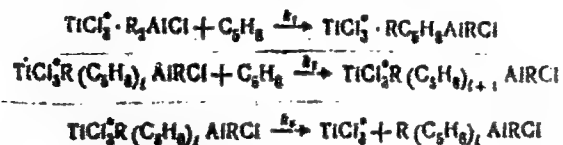
where: a is a proportionality coefficient, k_1 , k_2 , and k_3 are rate constants of

Card 2/3

L 50199-65

ACCESSION NR: AT5019602

the elementary steps of formation of active catalytic centers



n_0 is the actual initial isoprene concentration in the system in mol/L, n_0 is the total concentration of TiCl_3 molecules in mol/L, and K is the equilibrium constant of the isoprene polymerization reaction. The overall apparent activation energy of isoprene polymerization is 14 kcal/mol. For 25-90% conversion level, the actual kinetic expression for isoprene polymerization is

$$-\ln(1-x) = 2\beta \sqrt{\frac{D}{\pi}} \left(\frac{D}{\pi} \right)^{1/2} n_0^2 (\tau_{1/2}^2 - \tau_{1/2}^2)$$

where: x is fraction of converted isoprene, β is a proportionality coefficient, D is diffusion coefficient ($\text{mol} \cdot \text{cm}^2 \cdot \text{min}^{-1}$), $\tau_{1/2}$ and $\tau_{1/2}$ are initial and final instants of the polymerization reaction. In the case of isoprene polymerization in absence

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L 60199-65

ACCESSION NR: AT5019602

of a solvent, the depth of polymerization in the initial period (7-10% conversion) is proportional to time to the first power according to the formula

$$x = \frac{a \cdot k_1 \cdot k_2 \cdot K \cdot n_0^2}{k_3(1 + K n_0)} (t - t_0)$$

and the depth of polymerization in the subsequent diffusion-limited period is proportional to the square root of the initial and final reaction times according to the formula

$$x = 2\sigma \cdot \left(\frac{D}{\pi}\right)^{1/2} n_0^{1/2} (t^{1/2} - t_0^{1/2})$$

The polymer molecular weight is practically independent of conversion (depth of polymerization)--it increases with temperature and monomer concentration--and it is almost independent of catalyst concentration. The polymer microstructure is insensitive to changes in reaction temperature and to variations in monomer or catalyst concentration. Orig. art. has: 2 tables, 18 figures, and 10 formulas.

ASSOCIATION: none

SUBMITTED: 24Oct64

ENCL: 00

SUB CODE: MT,GC

NO REF SOV: 005

OTHER: 001

Card 3/3

ENT(m)/ENF(s)/ENG(n)/ENP(i)/Y Pc-1/Or-1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

Author: Potkov, A. A.; Marandzheva, Ye. N.; Khrenova, Z. A.

TITLE: Effect which contaminants in monomer and solvent have on kinetics of isoprene polymerization

SOURCE: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka. Polimerizatsiya izoprena kompleksnymi katalizatorami (Polymerization of Isoprene by Complex Catalysts). Moscow, Izd-vo Khimiya, 1964, ...

TOPIC TAGS: isoprene, polymerization, kinetics, inhibitor

ABSTRACT: Kinetics of isoprene polymerization was studied in the presence of 34 contaminants which are commonly encountered in commercial grade hydrocarbon solvents and commercial isoprene. These contaminants were: cyclopentadiene, dimethyl ether, mercaptan, vinyl acetylene, isopropyl acetylene, methyl allene, methylethyl acetylene, acetylene, diethyl sulfide, acetonitrile, diethyl amide, carbon monoxide, diethyl ether, vinylethyl ether, water, thiophene, carbon disulfide, carbon dioxide, COS, ethyl alcohol, acetone, methylethyl ketone, H₂S, O₂, HCOOH, NH₃, dimethyl amide, 2,6-dimethyl-octatriene-1,3,6, pentene dimer, piperylene, iso-

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L 47000-65

ACCESSION NR: AT5019603

butylene, trimethyl ethylene, methylethyl ethylene, and isopropyl ethylene. All experiments were conducted at 20°C in isopentane and petroleum ether solvents. The isoprene concentration was ~1.5 mol/l; the catalyst concentration was 0.008 mol/l; and the molar ratio of $Al(iso-C_4H_9)_3:TiCl_3 = 1:1$. Among the contaminants examined, pentane, dimethyl formamide butyl mercaptan, and acetylene derivatives were polymerization inhibitors. Mechanistically, two extreme cases were considered: (1) contaminant reacts primarily with the active polymer growth chains and does not interact with the active polymer growth chains, and (2) contaminant reacts with the active polymer growth chains and practically does not interact with the catalyst centers. Orig. art. has: 3 tables, 1 figure, 2 formulas.

ABSTRACT: none

EXPIRY: 24Oct64

ENCL: 00

SUB CODE: MT, GC

006

OTHER: 004

Card 2 2

L 60235-65

ADMISSION NR: AT5019604

UR/0000/64/000/000/0069/0081

AUTHOR: Korotkov, A. A.; Barsukova, M. N.

The action of catalytic poisons at various temperatures

ves yuznyy nauchno-issledovatel'skiy institut stateyneskogo kauchuka.
 (Izmena kompleksnykh katalizatorami isoprena by
 catalysts). Moscow, Izd-vo Khimiya, 1964, 20 p.

TOPIC TAGS: catalytic poison, polymerization, isopropyl acetylene, ethyl mercaptan, acetonitrile, catalysis

SUMMARY: Poisonous action of isopropyl acetylene, ethyl mercaptan, and aceto-
 nitrile on catalytic polymerization of isoprene was investigated kinetically at 100,
 150, and 200°C. Titanium trichloride generated from a mixture of triisobutyl alumi-
 num and titanium tetrachloride in 1:1 molar ratio served as polymerization catalyst.
 Acetonitrile was used as a solvent. The initial monomer concentration was 1.5 mol/l
 and the starting $TiCl_3$ concentration was 0.001 mol/l. According to the polymeriza-
 tion kinetics 1, mol % of isopropyl acetylene based on $TiCl_3$ reduced only slightly
 the initial rate of polymerization at 10°C, doubled the induction period, and gave

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ACCESSION NR: AT5019604

only 50% conversion as compared with the corresponding poison-free system. At 20°C, 4% isopropyl acetylene content was required to cause a decline in conversion to polymer (85% as compared with the poison-free system). At 30°C, no effect on conversion was observed up to 4 mol % of isopropyl acetylene (based on $TiCl_3$). The heat of activation of inhibition of growth of polymer chains by isopropyl acetylene is 6.7 kcal/mol and the activation energy of reaction of isopropyl acetylene with $\text{Ti}(\text{C}_2\text{H}_5)_3$ is 226,000 cal/mole. The heat of reaction of isopropyl acetylene with growing polymer chains, thus leading to termination of molecular weight, is about $150 \cdot 10^3$ (base case without $\text{Ti}(\text{C}_2\text{H}_5)_3$) kcal/mole. Acetylene and propyne acetylene poisons the polymerization system in quite nascently, whereas the polymer molecular weight is as large as it has been in the absence of a poison. The poisonous action of ethylene is similar but slightly less intense than that of isopropyl acetylene. The nature of the poisonous action of acetonitrile is different than that of the previous two poisons. Acetonitrile causes a substantial decline in the rate of polymerization reaction but it does not bring about any increase in the apparent induction period. Acetonitrile interacts relatively with the active centers of the catalyst, and it does not affect the polymer growth chains. Orig. art. has: 1 table, 4 figures, and 23 formulas.

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L 60245-05

ACCESSION NR: AT5019604

ASSOCIATION: none

SUBMITTED: 24Oct64

NO REF SOV: 006

ENCL: 00

OTHER: 004

SUB CODE: OC, GC

dm
Card 3/3

AUTHOR: Korotkov, A. A.; Kalinicheva, N. A.; Pichuzhkin, K. F.

TITLE: Effect of contaminants in titanium tetrachloride on the process of isoprene polymerization and the polymer properties

SOURCE: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka. Polimerizatsiya izoprena kompleksnymi katalizatorami (Polymerization of isoprene by complex catalysts). Moscow, Izd-vo Khimiya, 1964, 82-90

TOPIC TAGS: contaminant, titanium tetrachloride, isoprene polymerization, polymer property, Ziegler catalyst

ABSTRACT: The effect of contaminants commonly present in commercial grade titanium tetrachloride (CO_2 , SOCl_2 , POCl_3 , CS_2 , COCl_2 , SiCl_4 , and acetyl chlorides) on isoprene polymerization with Ziegler-type catalyst was studied at 25-30°C in an isopentane solvent. The polymerization mixtures contained 15 mol % isoprene based on isopentane solvent. The products were quenched with ethyl alcohol after 2 hours polymerization. The effect of individual contaminants was judged in terms of product characteristic viscosity and tensile strength of the vulcanized product samples measured at 20° and 100°C. A complex of TiCl_4 with $\text{Al}(\text{iso-C}_4\text{H}_9)_3$ served as a catalyst.

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L 60201-65
ACCESSION NR: AT5019605

It was found that HCl, $TiOCl_2$, CCl_4 , $SiCl_4$, $VOCl_3$, and $TiCl_4$ strongly inhibit isoprene polymerization even if present in very minute concentrations. HCl is the major contributor to the catalytically harmful action of the $TiOCl_2$ -HCl joint system (formed as a result of interaction of water with $TiCl_4$). The following $TiCl_4$ contaminants are little harmful: $FeCl_3$ up to 0.05 wt. %, $AlCl_3$ up to 0.05 wt. %, C_6Cl_6 up to 0.1 wt. %, and $SOCl_2$ up to 0.1 wt. %. Preparation of high activity complex polymerization catalyst requires freshly distilled high purity $TiCl_4$. Orig. art. has: 10 tables and 1 figure.

ASSOCIATION: none

SUBMITTED: 24Oct64

ENCL: 00

SUB CODE: IC, GC

NO REF SOV: 007

OTHER: 005

Card 2/2

L 60202-65 EWT(m)/EPF(c)/EWD(j)/T PC-4/Pr-4 GS/JAJ/RM
ACCESSION NR: AT5019606 UR/0000/54/000/000/0091/0100

AUTHOR: Korotkov, A. A.; Chevychalova, K. K.; Sorokina, N. I.

TITLE: Effect of contaminants in triisobutyl aluminum on the process of isoprene polymerization with a complex catalyst

SOURCE: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka. Polimerizatsiya izoprena kompleksnymi katalizatorami (Polymerization of isoprene by complex catalysts). Moscow, Izd-vo Khimiya, 1964, 91-100

TOPIC TAGS: contaminant, triisobutyl aluminum, isoprene, polymer, rubber, Ziegler catalyst

ABSTRACT: The effect of contaminants present in commercial grade triisobutyl aluminum (aluminum diisobutylchloride, salts of organic acids, aluminum diisobutylhydride, aluminum diisobutylisobutoxide, and isobutylene) on isoprene polymerization with Ziegler-type catalyst was studied at 20°C in an isopentane solvent. Isoprene concentration was 15-20 vol % based on reaction mixture and concentration of the catalyst was 3 wt % based on isoprene. After 2 hour polymerization the products were quenched with ethyl alcohol. The effect of individual contaminants was judged

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L 60202-65

ACCESSION NR: AT5019606

in terms of characteristic viscosity of the polymerization product and mechanical properties of vulcanized product samples as measured at 20° and 100°C. Up to 60 wt % of isobutylene and up to 1 wt % of aluminum butyl stearate (based on triisobutyl aluminum) has no effect on either the rate of isoprene polymerization or the rubber quality. Catalyst containing aluminum diisobutylisobutoxide, aluminum diisobutylchloride, and aluminum diisobutylhydride are less active and they give rubbers of inferior quality. Orig. art. has: 6 tables.

24Oct64

ENCL: 00

SUB CODE: OC,GC

NO REF SOV: 003

OTHER: 006

Card 2/2 *AR*

L 60203-65 EWT(m)/EPF(c)/EPR/EWP(j)/EWA(c) Pc-4/Pr-4/Ps-4 RPL WH/GS/JAJ/RM
 ACCESSION NR: AT5019607 UR/0000/64/000/000/0101/0111

AUTHOR: Petrov, G. N.; Korotkov, A. A.

TITLE: Reduction of vanadium trichlorooxide by organoaluminum compounds

SOURCE: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka. Polimerizatsiya izoprena kompleksnymi katalizatorami (Polymerization of isoprene by complex catalysts). Moscow, Izd-vo Khimiya, 1964, 101-111

TOPIC TAGS: reduction, complex catalyst, polymerization, organoaluminum, vanadium trichlorooxide

ABSTRACT: Reduction of VOCl_3 with R_3Al , R_2AlCl , RAlCl_2 , RAl(OR)_2 , $\text{R}_2\text{Al(OR)}$ and RAlCl(OR) at various component ratios, in argon atmosphere, was studied kinetically at 20°C , and in a benzene solvent; (R was C_2H_5). The experimental set-up is shown in fig. 1 of the Enclosure. Reaction mixtures were prepared from 0.1 molar benzene solutions of high purity reagents. R_3Al , R_2AlCl , and RAlCl_2 attack preferentially the V-O bond, RAlCl(OR) attacks preferentially the V-Cl bond, $\text{R}_2\text{Al(OR)}$ attacks both bonds equally, and RAl(OR)_2 does not react with VOCl_3 at all. Composition of the insoluble reaction product was calculated assuming a principle of equality of energy

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L 60203-65

ACCESSION NR: AT5019607

of formation of all possible complex compounds of aluminum alkyls with solid vanadium chlorides. Orig. art. has: 5 figures and 16 formulas.

ASSOCIATION: none

SUBMITTED: 24Oct64

ENCL: 01

SUB CODE: IC, GC

NO REF SOV: 004

OTHER: 003

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